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March 1981

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Some laser-induced reactions of BF_3, BCl_3 or $B(CH_3)_3$ with NF_3, N_2F_4 or C_2H_4 have been studied. These reactions were initiated by the multiphoton absorption of the infrared radiation from a cw CO_2 laser. In addition to numerous gaseous products, infrared spectra of solids, that have been identified as belonging to BF_4^- and BN, were observed. When possible, visible emission, which accompanied some of the reaction, was photographed. Analysis has shown it to be due, in

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part, to C_2 and CN when carbon was present and a continuum for a BCl_3 and N_2 mixture.

CONTENTS

I. INTRODUCTION

Dissociation of molecules from multiphoton absorption of infrared lasers has been well documented.[1,2] These laser-induced reactions can follow many channels to the final products. To be considered are the collisions between vibrationally excited species, radical reactions, thermal heating, and molecular rearrangement. By limiting some of these parameters, mechanisms of some laser-induced unimolecular reactions have been determined.[3,4] When another molecular species is added to the reaction, these mechanisms may no longer be favored.

The observation of intermediate radicals and final products is very important in the formulation of a reaction mechanism. In order to obtain some of this information, a number of experiments with boron containing compounds have been performed. The results of these experiments are reported herein.

II. EXPERIMENTAL

Commercially available tetrafluorohydrazine, nitrogen trifluoride, ethylene, boron trichloride and boron trifluoride were used in the experiments. The samples were used without further purification.

The reactions were carried out in a stainless steel cell (5x10 cm) equipped with O-ring seals for securing windows (5 cm diameter) onto the cells. ZnSe or KCl windows were used to pass the infrared beams and a Pyrex or sapphire window was used for monitoring the visible emission. Side reactions were observed when KCl and Pyrex windows were used.

A Coherent Radiation Laboratories Model 41 continuous-wave CO_2 laser in the range 10.4 to 9.4 μm provided the infrared laser excitation. The laser frequency being used was verified with an Optical Engineering CO_2 Spectrum Analyzer. Depending upon the laser line, output powers up to 150W could be obtained. The beam size measured from burn patterns was found to be approximately circular with a 4mm diameter.

The visible emission which was observed in some reactions was monitored photographically using a one-meter Czerny-Turner monochromator.

III. RESULTS

A series of Laser-Induced Chemistry (LIC) experiments have been performed in an attempt to produce refractory or propellant materials containing boron and to determine the reaction mechanism.

In an effort to produce NF_4BF_4, a mixture of BF_3 and N_2F_4 was irradiated. When a cell with KCl windows was used, a solid was produced which had a broad infrared band with peaks at 1030 and 1050 cm^{-1}. (See Figure 1.) This band agreed with the reported frequencies of the BF_4^- ion.[5-7] The corresponding NF_4^+ band was not observed.[8] When the windows were changed to ZnSe, a much weaker band was observed in the same frequency range. It was concluded

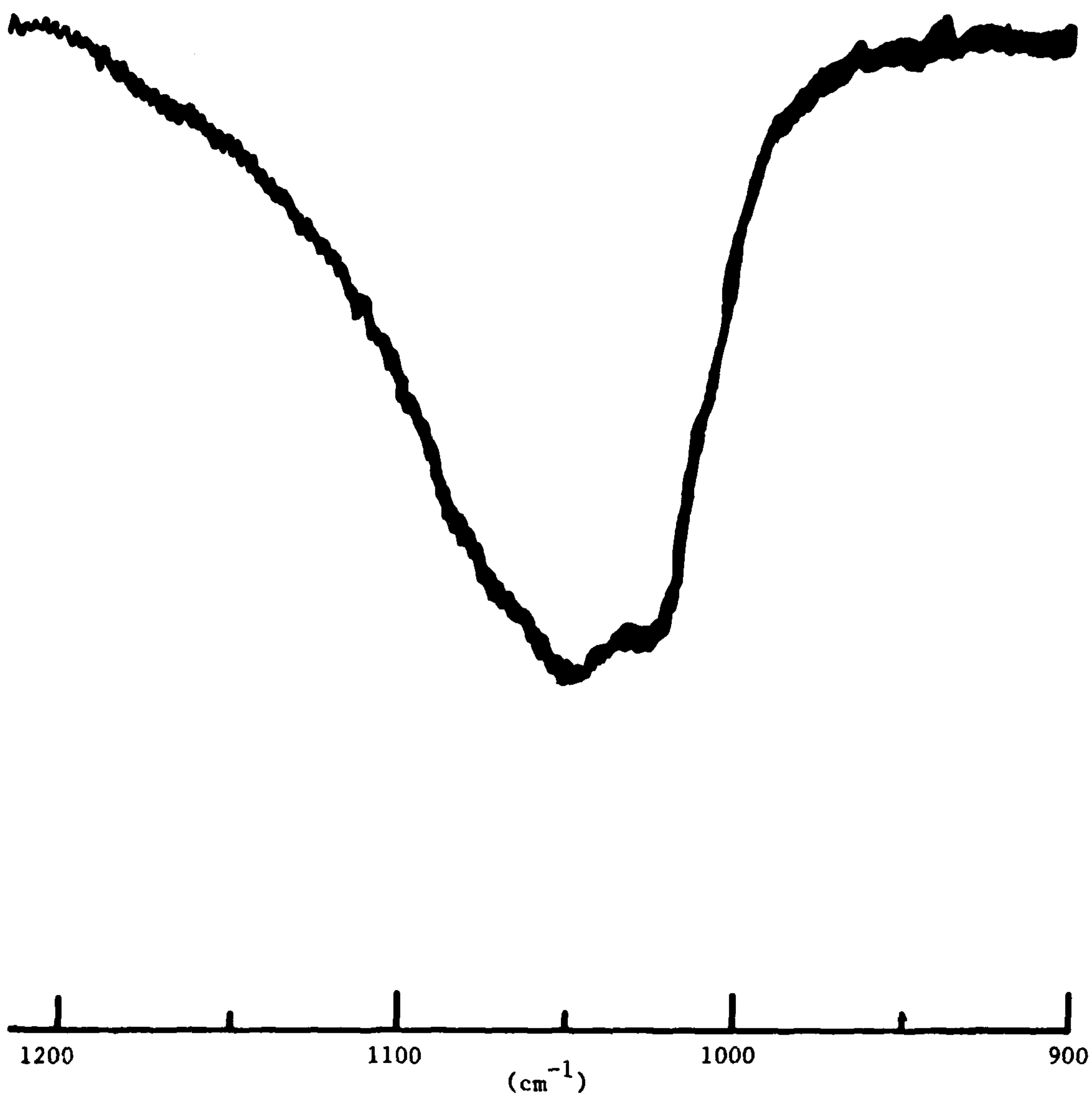

Figure 1. Infrared spectra of BF_4^- on KCl windows.

that the KCl was providing a surface for the BF_4^- to form and interact with a K^+ ion. This was further evidenced when it was observed, after the initial build-up of solid on the windows, that subsequent reactions produced only a small increase in solid.

A more energetic reaction was then attempted by using a mixture of BF_3, NF_3 or N_2F_4 and C_2H_4. When irradiated by the laser this mixture produced a visible flash. Except for different gaseous products and a deposit of carbon, the results were the same.

In the previous mixtures only the NF_3, N_2F_4, and/or C_2H_4 were being excited by the laser since the absorption frequencies of the BF_3 were outside the CO_2 laser frequencies. A reaction of BCl_3 and N_2F_4 was then performed since they could be simultaneously excited. A visible flash was also observed in this reaction but efforts to photograph the spectra were unsuccessful. The mole ratio was important in the products that were formed in these reactions. In a 1:1 ratio of BCl_3 and N_2F_4, only BF_3 was produced. When the ratio was changed to 1:2 BF_3, NF_3 and a solid were formed.

The infrared spectra of the solid showed two bands maximum at 960 and 1060 cm^{-1} (See Figure 2). The windows were ZnSe and only small amounts of BF_4^- had previously been observed on these windows. The frequency region of the bands was the same but the appearance of the bands was different from earlier observations. When the cell was opened to the air and a new spectra obtained, the band appearance had shifted and was the same as that previously observed for BF_4^-. This suggested that the BF_4^- was originally in a different crystalline configuration with a much larger crystal field effect than is normally observed.[5-7] The ZnSe windows were also observed to be pitted after these experiments.

Other product compounds of interest were BN and B_4C. Since the experiments to produce NF_4BF_4 contained boron, nitrogen, and carbon with no observation of these compounds, other reactant mixtures were needed.

One way to produce the ultraviolet spectra of BN is in a discharge through BCl_3 and N_2.[13] A mixture of these reactants gave an interesting visual display when the cell was irradiated. A greenish fluorescence was observed approximately 1 cm in diameter down the length of the cell. The recorded visible spectra showed only a continuum with no discernible band spectra.

After an intermittent exposure of the mixture for 1 minute, the infrared spectra indicated bands of a solid at 1265 and 720cm^{-1} (See Figure 3). These bands were in the correct frequency ranges for the stretching and bending modes of B-N.[9-11]

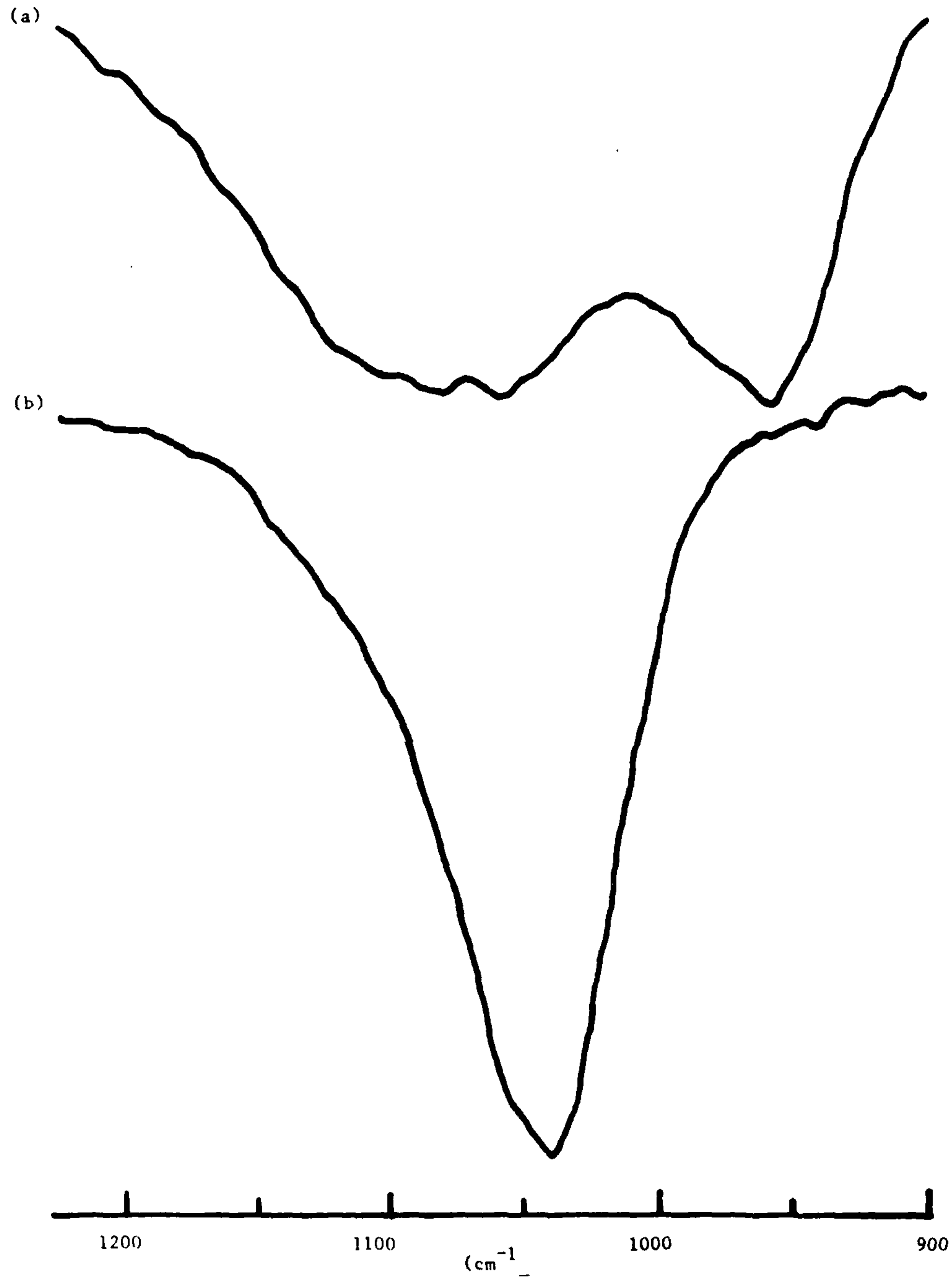

Figure 2. (a) Infrared spectra of product from BCl_3 and N_2F_4 reaction on ZnSe windows (8 cm^{-1} resolution); (b) Spectra of product in (a) after air was added to cell.

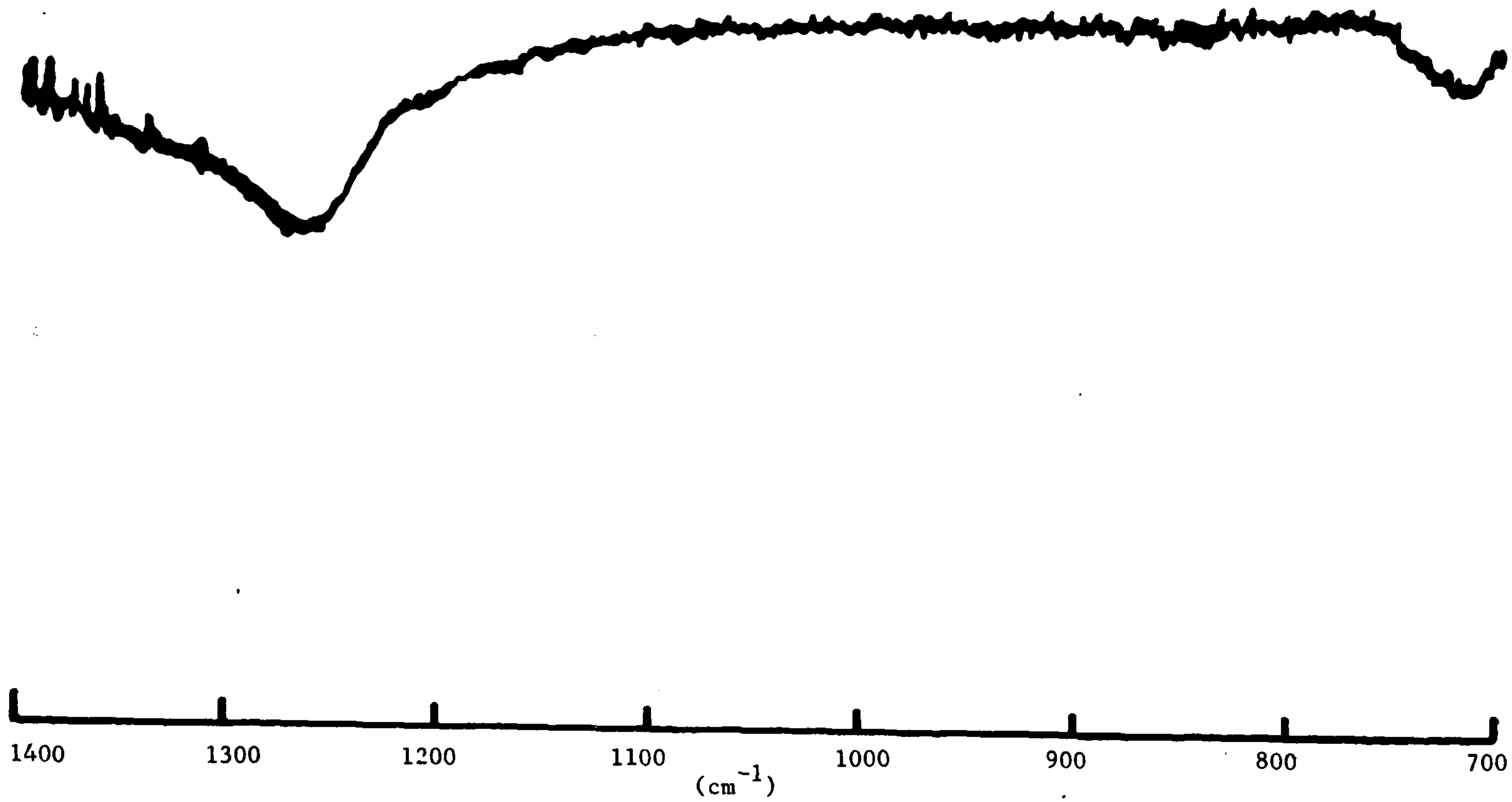

Figure 3. Infrared spectra of solid produced in BCl_3 and N_2 reaction.

In an attempt to produce B_4C a mixture of BCl_3 and C_2H_4 was subjected to 75W of P(14) $[00^01\text{-}10^00]$ radiation. The irradiated cell produced only a glow during exposure. The gaseous products were identified as C_2H_2[12], CH_4[12], HCl[14], and $HBCl_2$[15] (See Table 1). A weak absorption band of a solid was also observed with peaks at 1350 and 1265 cm^{-1}. This band was too high in frequency to belong to B_4C[10]. It has not been identified.

Another boron compound which has a resonant band with the CO_2 laser is trimethylboron. This molecule was reacted with NF_3 or N_2F_4. As shown in Table 1, the molecules produced in the reaction were dependent on the mole ratio. For the 1:1 and 2:1 mixtures of $B(CH_3)_3$ and NF_3, the results were the same. The gaseous products were C_2H_2, HCN[12], CH_4, HF, and a small amount of BF_3. No difference was noticed if the reaction was initiated by a resonant absorption of $B(CH_3)_3$ with the R(12) $[00^01\text{-}10^00]$ transition, or NF_3 with the P(48) $[00^01\text{-}10^00]$ transition. In a 1:2 mixture the products were C_2F_4[16], CF_4[17], C_2F_6[18], CF_3CN[19], CF_3H[20], HF[21] and BF_3. In a 1:2 mixture of $B(CH_3)_3$ and N_2F_4 the major products were CF_4 and HF, with small amounts of CF_3H and HCN. These products and ratios are consistent with results observed in reactions of NF_3 or N_2F_4 with ethylenes.[22] A black solid was observed on the walls of the cell which produced no infrared spectra. Reactions of carbon-containing compounds and NF_3 or N_2F_4 were always observed to produce varying amounts of carbon; however, the amount of BF_3 produced in these reactions could not account for all of the boron originally present.

A mixture of $B(CH_3)_3$ and N_2 was irradiated with powers up to 125W of the R(12) $[00^01\text{-}10^00]$ transition but no products were detected.

Part of the present task was to construct a HF/DF laser source from existing equipment. A vacuum system for a chemical laser cavity was erected and a dual 18-kilovolt power supply was connected to discharge tubes. In attempting to obtain lasing, it was established that the capacity of the vacuum pump was not large enough. After a delay a 100 l/min pump was connected to the system, which improved the flow of reactants, but the reactant mixture was still too nonhomogeneous for lasing to occur. It was decided to purchase a new laser cavity and delay the studies on the DF laser for the present.

IV. DISCUSSION AND RECOMMENDATION

Although the mechanism of these experiments may not be fully understood, these experiments have shown enough trends in product formation that product predictions of certain mixtures can be made.

TABLE 1. SUMMARY OF PRODUCTS FORMED IN THE LASER-INDUCED CHEMICAL REACTIONS

Reactants (mole ratio)	Major Products[1]	Laser Transition: Transition	Laser Transition: Frequency (cm^{-1})	Power (watts)	Window Materials
BF_3; N_2F_4 (1:1)	NF_3, BF_4^-, HCl	P(14)	949.48	75	KCl
BF_3; N_2F_4 (1:1)	NF_3, (BF_4^-)	P(14)	949.48	100	ZnSe
BF_3; N_2F_4 (1:2)	NF_3, BF_4^-, HCl	P(32)	932.96	100	KCl
BF_3; NF_3; C_2H_4 (1:1:1)	(CF_4), C_2H_2, HCN BF_4^-, HCl	P(32)	932.96	100	KCl
BF_3; NF_3; C_2H_4 (1:1:1)	C_2H_2, HCN, HF	P(40)	924.97	50	ZnSe
BF_3; N_2F_4; C_2H_4 (1:1:1)	C_2H_2, HCN, HF (BF_4^-)	P(40)	924.97	60	ZnSe
BCl_3; N_2F_4 (1:1)	BF_3	P(32)	932.96	65	ZnSe
BCl_3; N_2F_4 (1:2)	BF_3, NF_3, BF_4^-	P(32)	932.96	50	ZnSe
BCl_3; N_2 (2:1)	$HBCl_2$, HCl	P(14)	949.48	50	KCl
BCl_3; N_2 (2:1)	$HBCl_2$, HCl, BN	P(14)	949.48	100	KCl
BCl_3; N_2 (1:1)	BN	P(36)	929.01	100	KCl

[1] Compounds in parentheses were produced in very small amounts.

TABLE 1. (Concluded)

Reactants (mole ratio)	Major Products[1]	Transition	Laser Transition Frequency (cm^{-1})	Power (watts)	Window Materials
BCl_3; C_2H_4 (1:1)	C_2H_2, CH_4, HCl, $HBCl_2$	P(50)	914.43	70	KCl
BCl_3; C_2H_4 (1:1)	C_2H_2, CH_4, HCl, BCl_2 unknown solid	P(14)	949.48	75	KCl
BCl_3; C_2H_4 (2:1)	C_2H_2, CH_4, HCl, $HBCl_2$ unknown solid	P(14)	949.48	50	KCl
$B(CH_3)_3$; NF_3 (1:2)	C_2F_4, CF_4, C_2F_6, CF_3CN, CF_3H, BF_3, HF	P(48)	916.58	20	ZnSe
$B(CH_3)_3$; NF_3 (2:1)	CH_4, C_2H_2, HCN, (BF_3), HF	R(12)	970.55	90	ZnSe
$B(CH_3)_3$; N_2F_4 (1:2)	CF_4, (CF_3H), (HCN), HF	P(32)	932.96	50	ZnSe
$B(CH_3)_3$; NF_3 (1:1)	C_2H_2, HCN, CH_4, (BF_3), HF	P(48)	916.58	40	ZnSe
$B(CH_3)_3$; N_2 (1:1)	No reaction	R(12)	970.55	125	ZnSe

[1] Compounds in parentheses were produced in very small amounts.

In attempts to produce NF_4BF_4, it was found that BF_4^- could be generated by LIC. The BF_4^- formation was dependent upon having a surface which could supply a positive ion. NF_4^+ was apparently not stable under present experimental conditions although NF_3 was present after the reaction. More experiments are needed using other reaction mixtures and surfaces to determine if NF_4^+ can be generated by LIC.

The infrared bands (1265 and 720 cm^{-1}) observed for the solid formed in the BCl_3 and N_2 reaction are interesting. They do not agree with either hexagonal[9,10] (1390 and 810 cm^{-1}) or cubic (1100 and 700 cm^{-1}) BN.[11] This solid is apparently some form of BN but its exact nature is unclear.

Although some BN was produced it was not very cost effective in terms of the high laser power inputs for the small amount of BN formed. A reaction mixture that would have been ideal is BF_3 and NH_3; however, these components react on mixing to form BF_3NH_3. One way around this could be to irradiate the gases as they mix in a flow system. Another technique could be to irradiate the solid BF_3NH_3. Experiments in these directions are needed.

The reaction of $B(CH_3)_3$ and NF_3 produced no new products. The only interesting feature of this reaction was the disappearance of the boron from the infrared spectra. The most probable explanation is that pure boron was formed and settled out with the carbon that was also formed. There was no indication of any B_4C having been formed, but a closer look at this precipitate is needed.

In all reaction mixtures, (except for BF_3) that contained N_2F_4 or NF_3, irradiation above threshold power produced a bright flash. In order to understand some of the intermediate products this visible emission was spectrally analyzed. The spectra of mixtures containing carbon and nitrogen compounds always showed a continuum overlapped by band structure of CN and C_2.[13] This spectra could always be photographed from a single reaction. In the mixture of BCl_3 and N_2F_4 the flash was not intense enough to obtain the spectra.

In mixtures that contain BCl_3, glows were observed. These were weak in intensity except for the BCl_3 and N_2 reaction. The spectra from reaction, as indicated earlier, indicated only a continuum. The exact nature of this continuous emission has not been determined.

A study that might prove very helpful in determining intermediate radicals, would be the analysis of the infrared emission produced in these reactions.

The laser-induced reaction containing fluorine, in general, goes to completion. This gives off a considerable amount of energy which is the driving force that produces the observed chain reactions. In this environment are produced only the most thermodynamically stable products for a given stoichiometric mixture. In general these products are relatively small molecules.

These experiments have shown that products formed in reactions can be controlled, to a certain extent, by the initial mixture parameter at ambient temperatures, but much more work is needed to obtain the most efficient parameters. Until a better understanding of the mechanisms that drive reaction of mixtures is obtained, many more fundamental experiments are needed in laser-induced chemistry.

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